Uptake of Methanol Vapor in Sulfuric Acid Solutions

Sean M. Kane and Ming-Taun Leu*

Earth and Space Sciences Division, Jet Propulsion Laboratory,

California Institute of Technology, Pasadena, CA 91109

Abstract

The uptake of gas-phase methanol by liquid sulfuric acid has been investigated over the composition range of 40 - 85 wt % H_2SO_4 and between the temperatures of 210-235 K. Laboratory studies were performed with a flow-tube reactor coupled to an electron-impact ionization mass spectrometer for detection of trace gases. While reversible uptake was the primary mechanism at low acid concentrations, irreversible reaction between methanol and sulfuric acid at low temperatures, forming methyl hydrogen sulfate and dimethylsulfate, was observed at all concentrations. Above 65 wt % H_2SO_4, more than 90 % of uptake was found to be reactive. On the basis of the uptake data and the calculated liquid-phase diffusion coefficients, the product of the effective Henry's law constant (H^*) and the square root of the overall liquid-phase reaction rate (k_l) was calculated as a function of acid concentration and temperature. Implications to atmospheric chemistry in the upper troposphere are briefly discussed.

* Author to whom correspondence should be addressed.

Introduction

Oxygenated hydrocarbons, particularly acetone, play an important role in atmospheric chemistry by contributing the production of HO_x free radicals and consequently increasing the formation of ozone in the upper troposphere.[1] Although methanol is considered to be of secondary importance in these aspects, the concentration of methanol has been found to be as high as 700 ppt at 5-10 km.[2,3] Hence, it is important to investigate the production and loss mechanisms of methanol in the atmosphere. Sources of methanol in the atmosphere include secondary reactions of hydrocarbons, biomass burning, and direct biogenic and anthropogenic emissions.[4] On the other hand, photolytic loss of methanol is believed to be insignificant.[5] Moreover, reaction with ice particles inside cirrus cloud is also very slow.[6] It has been thought that the only significant loss mechanism for methanol in the upper troposphere is the reaction with hydroxyl radicals. However, heterogeneous reaction of methanol in liquid sulfuric acid has not, to this point, been considered.

Sulfate aerosols are thought to be the dominant form of aerosol in the upper troposphere. Very recently organic acids and hydroxymethanesulfonic acid (HMSA) have been identified in-situ in aerosols at an altitude of 5 to 19 km.[7] These organic-containing aerosols are particularly more pronounced in the tropics because of convection from the troposphere. Thus, it is intriguing to understand their formation mechanism, for example, the interaction of gas-phase organic compounds with liquid sulfuric acid.

In the upper troposphere, sulfate aerosols are mainly composed of between 40-80 wt % H_2SO_4 and ambient temperatures are in the range of 200-260 K.[8,9] In order to

2

understand the possible importance of this system, we have examined the uptake and reactivity of methanol in liquid sulfuric acid over temperature and acid concentration ranges in the upper troposphere and lower stratosphere.

Experimental Method

Apparatus: Uptake measurements in this experiment were performed using a fast flow-tube reactor coupled with an electron-impact ionization mass spectrometer, which has previously been described in detail.[10,11] The reactor made of Pyrex tubing was 25 cm long with an inner diameter of 1.8 cm. The bottom of the reactor was recessed to form a trough (1.9 cm wide and 0.3 cm deep) which held the liquid sulfuric acid. Temperature during experiments was controlled by flowing cold methanol through the outer jacket of the reactor. Helium carrier gas was admitted through a sidearm inlet, while methanol in another helium carrier was added by a movable Pyrex injector. Pressures in the reactor were monitored by a high-precision capacitance manometer (MKS Instruments, Model 390 HA, 10 Torr full scale). Typically, a total pressure of 0.47 Torr was used.

Materials: Methanol (*Fisher Scientific, 99.9 %, Reagent Grade*) was used as received without further purification and its purity was confirmed by the mass spectrometer. A sample vial containing the methanol was placed in a methanol/ dry ice bath in order to control the concentration of methanol inside the reactor. The partial pressure of methanol used in these experiments were in the range of 1.7×10^{-4} to 1.7×10^{-6} Torr, depending on the type of experiment performed. Helium (Matheson Gas Company, 99.999 %, Ultrahigh Purity Grade) was used as shipped for both the methanol

carrier gas and main flow gas. Sulfuric acid solutions of known compositions were prepared by dilutions of 96.2 wt % H_2SO_4 (J. T. Baker Chemical Co.) with distilled water. To ensure a constant composition of H_2SO_4 over a long period of time, the helium flow gas was humidified in a vessel with the same H_2SO_4 composition and temperature as the reaction cell. Additionally, the acid reservoir was changed frequently and the composition of the acid was checked before and after each set of experiments by determining the density of the acid solutions as an expedient method to check H_2SO_4 composition.[12]

Data Analysis: Uptake coefficient was determined from the methanol data according to the equation: [10,11]

$$\gamma = \frac{4k_c}{\omega}\left(\frac{V}{S}\right) \tag{1}$$

where V is the volume of the reaction cell, S is the geometric area of the acid reservoir, ω is the mean thermal speed of the molecule, and k_c is the corrected first-order rate coefficient. This rate coefficient is related to the fractional change of the gas-phase concentration of methanol, calculated by: [10,11]

$$k_c = k_g(1 + kD_g/v^2) \tag{2}$$

where D_g is the diffusion coefficient of methanol in He ($D_g = 424/p$ Torr cm^2 s^{-1} at 295 K), and v is the average flow velocity. A temperature dependence of $T^{1.75}$ was used for estimation of D_g at other temperatures. The observed first order rate, k_g, is calculated by the equation:

$$k_g = \frac{F_g}{V}\left(\frac{\Delta n}{n}\right) \tag{3}$$

where F_g is the carrier gas flow rate, and $(\Delta n/n)$ is the fractional change in the gas-phase concentration of methanol after exposure to sulfuric acid by moving the sliding Pyrex injector. Since a symmetrical, cylindrical tube was not used for the uptake coefficient measurements, correction for radial gas-phase diffusion was not taken into account in the determination of k_g because this correction was considered to be rather imprecise. However, we estimate that this correction is very small, less than 10 %.

Under conditions where less than 10% of methanol is reversibly absorbed (for example, the experiments using 65 wt % H_2SO_4 or greater, see the next section), the observed uptake coefficient can be approximately represented by the reactive uptake coefficient:

$$\gamma = \frac{4RTH^* \sqrt{k_l D_l}}{\omega} \tag{4}$$

where R is the gas constant (0.082 L atm mol^{-1} K^{-1}), T is temperature, H* is the Henry's Law solubility constant, D_l is the liquid diffusion constant and k_l is the overall rate constant for liquid-phase reactions. Using Eq (4), we are able to derive $H^*k_l^{1/2}$ from γ. The details are given in the later section.

Liquid-Phase Diffusion Coefficients: The determination of the liquid phase diffusion coefficient was performed using the method suggested by Klassen et al.[13] The diffusion coefficient of methanol in liquid sulfuric acid is given by

$$D_l = \frac{c T}{\eta} \tag{5}$$

where T is the temperature, η is the viscosity of sulfuric acid, and c is a constant determined from the molar volume of methanol (Le Bas additivity rules). Wilke and Chang [14] empirically determined the value c for the species in liquid sulfuric acid,

$$c = \frac{7.4 \times 10^{-8} (\kappa_{solvent})^{1/2}}{V_A^{0.6}} \qquad (6)$$

where $\kappa_{solvent}$ is a solvent dependent empirical factor ($\kappa_{solvent} = 64$) [15] and V_A is the Le Bas molar volume of solute A (methanol) at its normal boiling temperature ($V_A = 37$ cm^3/mol).[15] We calculated c to be 6.78×10^{-8} for methanol in H_2SO_4. In general, D_l decreases with decreasing temperature and increasing acid concentration. It is noted that the square root of D_l is used in the determination of $H^*k_l^{1/2}$ and thus the error associated with the procedure of D_l estimation is about 10-20%.

Results and Discussion

Methanol is found to exhibit some level of irreversible uptake at all concentrations examined, and requires a long time to reach equilibrium at concentrations dominated by reversible uptake. A relatively high pressure of methanol (1.7×10^{-4} Torr) was used in these experiments to facilitate the rate at which equilibrium of methanol with liquid sulfuric acid could be reached. A representative set of methanol uptake experiments is shown in figure 1. The uptake and desorption of methanol is performed at 213.1 K for 40-85 wt %. While 40 wt % H_2SO_4 shows significant low temperature methanol desorption, only trace amounts of methanol were observed at 75 wt % and no desorption occurred from 85 wt % H_2SO_4 at 213.1 K. To further identify the components in the sulfuric acid following methanol exposure, samples were heated to room temperature after the methanol flow was shut off and baseline level was achieved. The heating curves for each experiment are indicated by the dotted lines, with the temperature on the right axis. Only 75 wt % H_2SO_4 shows significant high temperature desorption upon heating, although all samples examined did exhibit some methanol desorption.

While a small methanol desorption at high temperature is expected from 40 wt % H_2SO_4 since the majority of exposed methanol was reversibly absorbed, the low yield from 85 wt % H_2SO_4 suggests a further reaction than that observed at 75 wt % that is not thermally reversible at these conditions.

In order to better identify the reversible and reactive components of methanol uptake by H_2SO_4, the desorbing fractions of methanol were determined both at 213.1 K and following heating to room temperature for a range of acid concentration (40-85 wt %). The desorbing fractions of methanol are shown for low temperature (upper panel) and high temperature (lower panel). The low temperature data supports an acid-dependent reactive component for methanol absorption. As acid concentration increases, the low temperature (non-reactive uptake) methanol fraction decreases from 0.50 at 40 wt % H_2SO_4 to none at 85 wt % H_2SO_4. Thus, under constant temperature conditions it is approximately 50% physical uptake for 40 wt % H_2SO_4. The desorbing methanol fraction, from heating to room temperature (lower panel), increases from 0.25 for 40 wt % to a peak at 75 wt %, followed by a steep drop at higher concentrations. The most likely reaction of methanol and sulfuric acid would be the formation of methyl hydrogen sulfate (MHS) [16-20]

$$CH_3OH + H_2SO_4 \rightarrow CH_3SO_4H + H_2O \qquad (7)$$
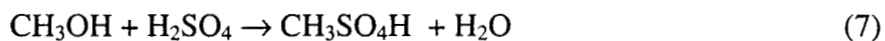
While this product was not directly observable under the flow tube experimental conditions, a series of experiments were conducted by mixing liquid methanol with H_2SO_4 from 40 to 85 wt % at room temperature and monitoring reaction products by mass spectrometry. Figure 3 shows the results for 75 wt % at 295 K. Peaks at m/e = 112 (the parent mass of methyl hydrogen sulfate) and 97 and 81 (fragment peaks for loss of

methyl and methoxy respectively) demonstrate that MHS is a reasonable reaction product for reaction at low temperature. The change in the curve above 75 wt % suggests that a second reactive mechanism occurs at higher acid concentration. As this reaction is not readily reversible at room temperature, it is most likely the further reaction of methyl hydrogen sulfate with methanol to produce dimethylsulfate [21,22]

$$CH_3SO_4H + CH_3OH \rightarrow (CH_3)_2SO_4 + H_2O \qquad (8)$$
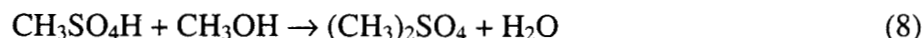
Low vapor pressure prevents direct observation of this product even in the mixed liquid experiments. This reaction mechanism is in good agreement with the chemistry observed by Hanson et al. [19]

As discussed in the experimental section, the fractional change in methanol signal can be used to determine the uptake coefficient for methanol on sulfuric acid. For acid concentrations above 65 wt %, all uptake can be considered irreversible. As reactive uptake does not exhibit a recovery curve (similar to the profile of 40 wt % in figure 1), the fractional change in methanol signal is acquired by a step-wise increase in the distance the glass injector is pulled into to reaction cell, allowing sufficient time between each step to collect a good signal.[23] To better simulate atmospheric conditions in these experiments, the partial pressure of methanol was reduced to approximately 2×10^{-6} Torr. For each of three acid compositions, the value of γ was determined over a temperature range of 210-235 K. The results are plotted in figure 4, with linear regressions of these data and each curve plotted separately. While the range of γ values is clustered between 0.012 to 0.023 in the range of concentrations and temperature observed, a general trend can be observed. At very cold temperatures (~210 K), the values for γ are the same regardless of acid concentration. As temperature increases,

however, γ decreases for 65 wt % H_2SO_4, while it increases for 75 and 80 wt %. This also suggests a change in the reaction mechanism involved in uptake, as discussed above.

Approximating methanol uptake by 40 wt % sulfuric acid allows an estimate of H^* to be found by methods described elsewhere.[23] In the temperature range of 210 – 230 K, H^* ranges from 5.2×10^4 to 1.2×10^6 M/atm. These values neglect the reactive components of uptake, providing a lower limit for methanol solubility in the acid. For concentrations about 65 wt %, almost all uptake is reactive and thus the atmospherically important values of H^* and k_l can be determined from Equation 1. Initially, these values are presented as a product. Figure 5 shows the results for the calculation of $H^*k_l^{1/2}$ or acid concentrations between 65-80 wt %. The combined product is found to increase with acid concentration and decrease as a function of temperature.

To our knowledge, the effective Henry's law constant has not been measured for acid compositions between 65-80 %. The determination of k_l can be made by assuming the Henry's law constant of methanol is approximately that of the value for methanol in water (based on the similar pK_a values of methanol and water).[24] The assumption is further supported by the evidence that the solubility of peroxyacetyl nitrate (PAN) in liquid sulfuric acid is nearly equal to that in water.[25] The equation for H^* of methanol in water [26-28] is

$$\ln(H^*) = \ln [K_{H(T_0)}] + (\Delta H_0/R)(1/T_0 - 1/T) \tag{9}$$

where $\ln [K_{H(T_0)}] = 5.39$, $\Delta H_0/R = -4900$ K, and $T_0 = 298.15$ K. The overall rate constant for methanol in H_2SO_4 based on this assumption is shown in figure 6. Reaction rate increases as acid concentration increases in the temperature ranges examined. For 65 and 75 wt % H_2SO_4, which exhibited thermal reversibility as shown in figure 2, show an

increasing reaction rate with increasing temperature. The data collected at 80 wt %
H_2SO_4, however, shows a nearly constant reaction rate with respect to temperature. This
also supports the further reaction of methanol and sulfuric acid to dimethylsulfate,
Reactions (7) and (8), in this acidity range. The overall reaction rate, k_l, in the range of
$0.1 - 10 \ s^{-1}$ suggests that it is potentially important in the upper troposphere.

Atmospheric implications

In order to illustrate the atmospheric importance for the reaction of methanol in
sulfuric acid, we need to detail the loss mechanisms and their reaction rates for typical
atmospheric conditions. As noted in the Introduction Section, photodissociative loss of
methanol has been found to be insignificant.[5] Reactions with liquid water or ice are
also found to be very slow.[6] In addition to the reaction mechanism we have suggested
here, the only other significant loss mechanism for methanol is reaction with OH radical.
The estimated reaction rate for $OH + CH_3OH \rightarrow CH_3O + H_2O$ at 10 km is $k(OH +
CH_3OH) \times [OH] = 1.5 \times 10^{-7} \ s^{-1}$. The rate coefficient is taken from the recommendation
of NASA Data Evaluation Panel Report [28] and the average OH concentration is
assumed to be 3×10^5 molecules/cm^3.[28] To calculate the loss rate of methanol due to
the reaction with sulfuric acid, we estimate the first-order rate to be $(1/4)\gamma\omega A$. The γ
value is adopted from the data for 75 wt % H_2SO_4 reported in the previous section. We
assume the surface area density of sulfate aerosol at an altitude of 10 km is about 2×10^{-7}
cm^2/cm^3 for volcanic-perturbed conditions and 1×10^{-8} cm^2/cm^3 for quiescent conditions,
respectively.[29,30] By using the mean thermal velocity for methanol, ω, at 220 K, the
rate is estimated to be $4 \times 10^{-5} \ s^{-1}$ under perturbed volcanic conditions and $2 \times 10^{-6} \ s^{-1}$
under quiescent conditions, respectively. Although the estimation is somewhat crude,

we conclude that the reaction with sulfuric acid is the dominant loss mechanism of methanol in the upper troposphere. The potential impact of our findings on the production of hydroxyl radicals and ozone perturbation in the upper troposphere should be assessed by the atmospheric model and is beyond the scope of this article.

References

(1) Wennberg, P. O.; et al. *Science* **1998**, *279*, 49.

(2) Singh, H. B.; et al. *J. Geophys. Res.* **1994**, *99*, 1805.

(3) Singh, H. B.; Kanakidou, M.; Crutzen, P. J.; Jacob, D. J. *Nature* **1995**, *378*, 50.

(4) Holzinger, R.; et al. *Geophys. Res. Lett.* **1999**, *104*, 1705.

(5) Harrison, A. J.; Cederholm, B. J.; Terwilliger, M. A. *J. Chem. Phys.* **1959**, *30*, 355.

(6) Zondlo, M. A.; Warshawsky, M. S.; Tolbert, M. A., 1998 AGU Fall Meeting in San Francisco, Paper Number A12C-01.

(7) Murphy, D. M.; Thomson, D. S.; Mahoney, M. J. *Science*, **1998**, *282*, 1664.

(8) "Scientific Assessment of Ozone Depletion: 1994", World Meteorological Organization, Global Ozone Research and Monitoring Project-Report No. 37, Chapter 3.

(9) Steele, H. M.; Hamill, P. *J. Aerosol Sci.* **1981**, *12*, 517.

(10) Leu, M.-T.; Timonen, R. S.; Keyser, L. F.; Yung, Y. L. *J. Phys. Chem.* **1995**, *99*, 13203.

(11) Choi, W.; Leu, M.-T. *J. Phys. Chem.* **1998**, *102*, 7618.

(12) Handbook of Chemistry and Physics, 65th Edition, CRC Press, 1984.

(13) Klassen, J. K; Hu, Z.; Williams, L. R. *J. Geophys. Res.* **1998**, *103*, 16197.

(14) Wilke, C. R.; Chang, P. *AlChE J.* **1995**, *1*, 264.

(15) Reid, R.C.; Prausnitz, J. M.; Poling, B.E. *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1987.

(16) Liler, M. *Reaction Mechanisms in Sulphuric Acid and Other Strong Acid Solutions*, Academic Press, New York, 1971.

(17) Vinnik, M. I.; Kislina, I. S.; Kitaigorodskii, A. N.; Nikitaev, A. T. *B. Acad. Sci USSR Ch.* **1986**, *35*, 2447.

(18) Almstead, N.; et al. *Tetra. Lett.* **1987**, *28*, 1627 .

(19) Hanson, L. D.; White, V. F.; Eatough, D. J. *Environ. Sci. Technol.* **1986**, *20*, 872.

(20) Japar, S. M.; Wallington, T. J.; Andino, J. M.; Ball, J. C. *Environ. Sci. Technol.* **1990**, *24*, 313.

(21) Deno, N. C.; Wisotsky, M. J. *J. Amer. Chem. Soc.* **1963**, *85*, 1735.

(22) Deno, N. C.; Newman, M. S. *J. Amer. Chem. Soc.* **1950**, *72*, 3852.

(23) Kane, S. M.; Timonen, R. S.; Leu, M.-T. *J. Phys. Chem.* **1999**, *103*, 9259.

(24) Fox, M. A.; Whitesell, J. K., *Organic Chemistry,* Second Edition, Jones and Bartlett Publishers, Sudbury, Massachusetts (1997)

(25) Zhang, R.; Leu, M.- T. *J. Geophys. Res.* **1997**, *102*, 8837.

(26) Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill Book Company, New York (1970).

(27) Snider, J. R.; Dawson, G. A. *J. Geophys. Res.* **1985**, 90, 3797.

(28) DeMore, W. B.; et al., Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, JPL Publication 97 - 4.

(29) Scientific Assessment of Ozone Depletion: 1998; Global Ozone Research and Monitoring Project-Report No. 44; World Meteorological Organization, Geneva, Switzerland; Chapter 3.

(30) Aviation and the Global Atmosphere, Cambridge University Press (1999), p.72.

Figures Captions

Figure 1. Uptake and desorption of methanol at 213.1 K, followed by heating to room temperature, for 40, 75, and 85 wt % H_2SO_4 (chosen as most representative data). Heating curves for each experiment are indicated by the dotted lines, using the right axis. 40 wt % H_2SO_4 shows significant low temperature methanol desorption, with only trace amounts of methanol observed at 75 wt % and no desorption occurred from 85 wt % H_2SO_4 at 213.1 K. Once methanol flow was shut off and baseline level was achieved, samples were heated to room temperature.

Figure 2. For methanol uptake at 213.1 K on a variety of sulfuric acid concentrations the low temperature (upper panel) and high temperature (lower panel) fractions of desorbing methanol are shown. As acid concentration increases, the low temperature (non-reactive uptake) desorption fraction decreases from ~0.5 at 40 wt % H_2SO_4 to none at 85 wt %. High temperature (thermally reversible reactive uptake) desorption increases from 0.25 for 40 wt % to a peak at 75 wt %, followed by a steep drop at higher concentration. The steep drop, plus the total desorbing fraction being below 0.75, suggests a second reaction that is irreversible under the experimental conditions examined.

Figure 3. Mass spectrum from mixing of 15 ml H_2SO_4 with 10 ml methanol in vacuum. Peaks at m/e 112 and 97 indicate formation of methyl hydrogen sulfate (MHS) under these conditions. Additional peaks may be attributed to either MHS or sulfuric acid.

14

Figure 4. Calculated values for γ plotted against temperature for 65-80 wt % H_2SO_4. γ values range from 0.01 to 0.023 in the range of concentrations and temperature observed. Solid lines are linear regression fits to the data.

Figure 5. Determination of $H*k_1^{1/2}$ for 65-80 wt % H_2SO_4. The combined product is found to increase with acid concentration and decrease as a function of temperature. See text for details.

Figure 6. Rate constant for methanol uptake by 65, 75, and 80 wt % H_2SO_4. While 65 and 75 wt % shows similar temperature dependence, k_1 for 80 wt % is independent of temperature, indicating a different overall reaction than that observed for the lower acid concentrations.
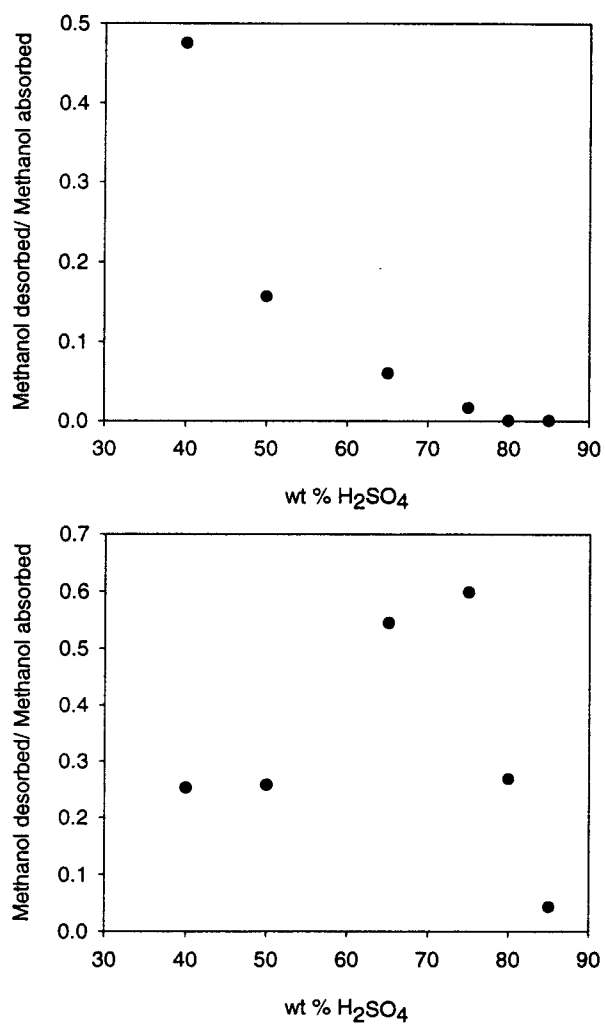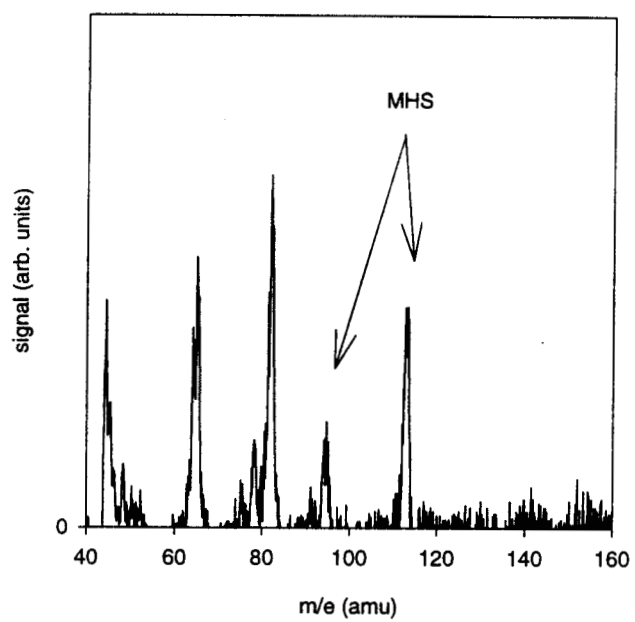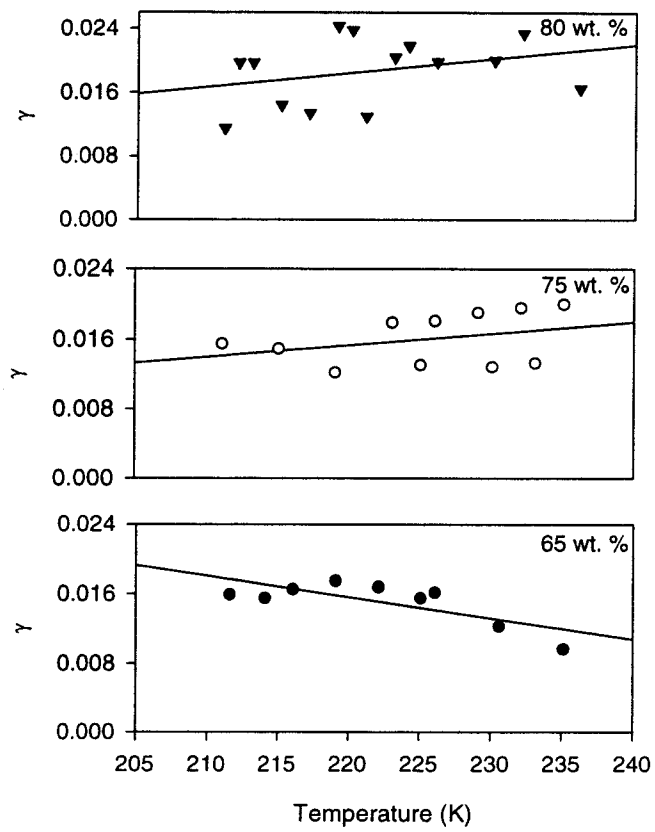
Figure 1
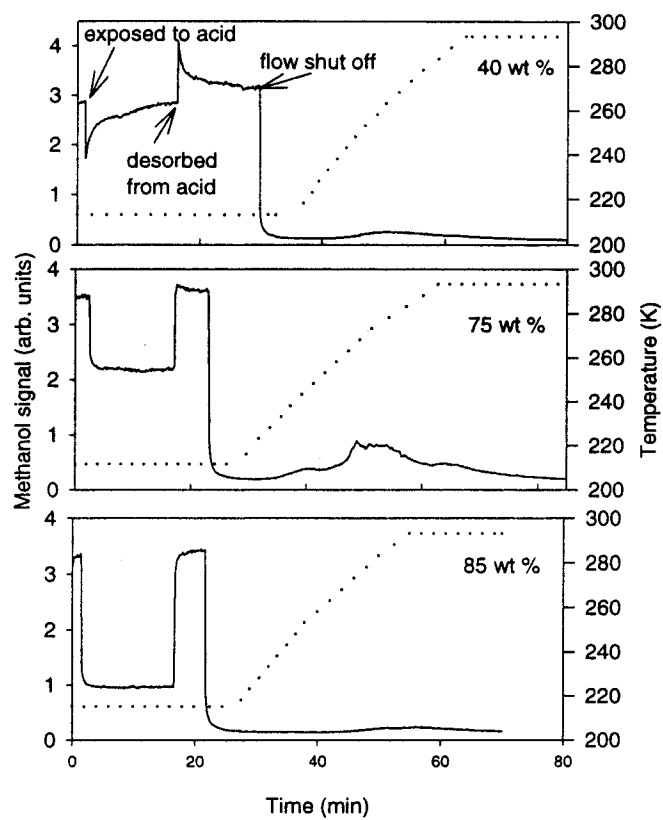
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6